Attachment to Paper No. 4
09/881,574

(12) UK Patent Application (19) GB (11) 2 014 870 A

(21) Application No. 7906442
(22) Date of filing 23 Feb 1979
(23) Claims filed 23 Feb 1979
(30) Priority data
(31) 880804
(32) 24 Feb 1978
(33) United States of America (US)
(43) Application published 5 Sep 1979
(51) INT CL²
B01D 19/00
(52) Domestic classification
B1M 2 X
(56) Documents cited
GB 1440963
GB 1382933
(58) Field of search
B1L
B1M
B1X
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(54) **Degasser**

(57) Gases are removed from liquids through a semipermeable membrane comprising a fluorinated polymer containing the substituent -SO_3H or a salt thereof attached to fluorinated carbons, eg. a copolymer of tetrafluoroethylene and perfluoro (3,6-dioxa-4-methyl-7-octenesulphonyl fluoride) in which the sulphonyl fluoride group is hydrolysed -SO_3H or a salt thereof.

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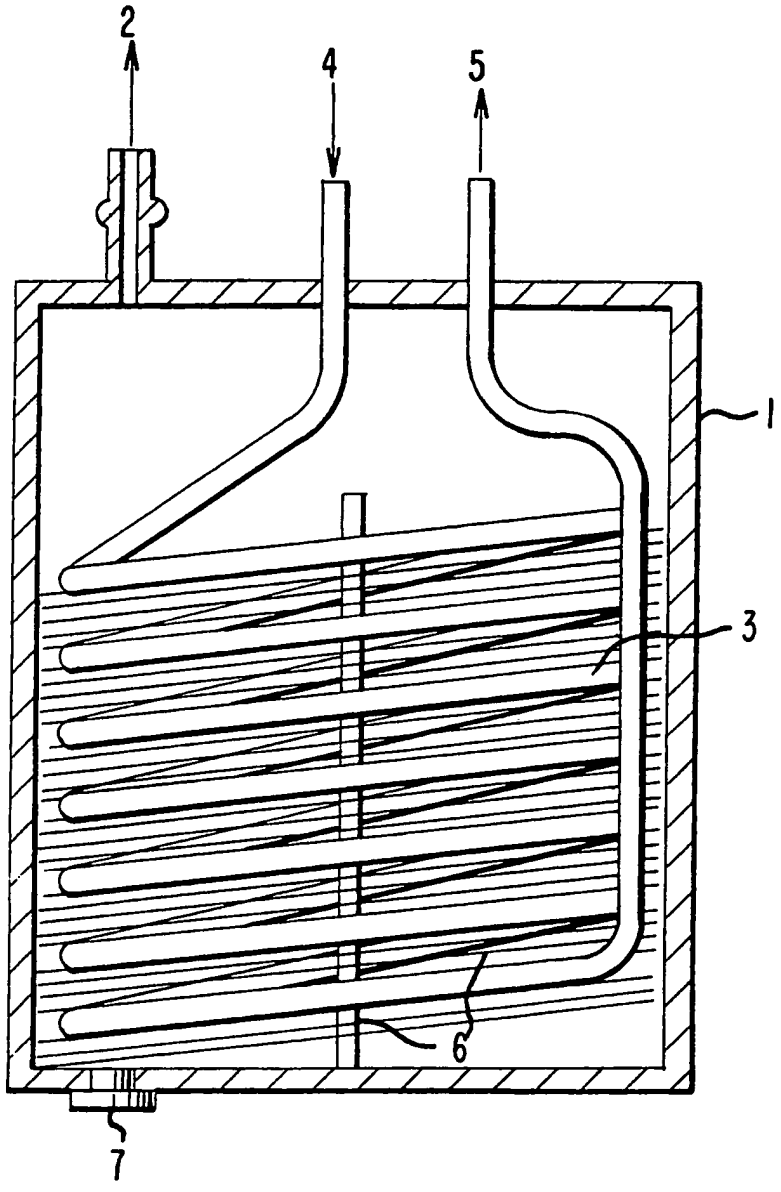
FIG. 1



SPECIFICATION

Degasser

This invention relates to a device for removing dissolved gases and gas bubbles from a solvent. Such devices are particularly useful in liquid chromatography systems.

Operators of liquid chromatography systems have recognized problems such as disruption of flow patterns and detector errors caused by the formation of gas bubbles in the system. These bubbles form in liquid chromatography systems because of changes in the solubility of gases in the solvents used in the system. For example, temperature changes within the column or mixing solvents within the system change gas solubility in the liquids and can generate bubbles. Attempts to overcome this problem include the use of degassing devices having a semipermeable membrane through which gas is diffused from the liquid. In order for such devices to be effective, the membranes used must be chemically inert with respect to the solvents in the system; they must be capable of transferring a sufficient amount of gas to prevent the formation of or removal of bubbles from the system; and they must be strong enough to withstand the pressure applied to the liquid in the system. The membranes available to this point have not had a favourable combination of these three properties. This invention provides a membrane which is inert in many chemical systems, has surprisingly high gas transfer characteristics and is strong enough to withstand normal operating pressures.

Degassers using the membrane of this invention are efficient enough to remove or prevent the formation of bubbles large enough to disrupt flow patterns or cause detector errors with a liquid chromatograph. It has also been found that the degassers can decrease the dissolved gas concentration to a point where normal liquid chromatograph pump performance is improved. This is thought to be the result of prevention of the formation of minute bubbles at points of turbulence within the pump and check velves systems. The use of degassers of this invention is not limited to liquid chromatography systems. The devices will be similarly useful in any system requiring the removal of dissolved gas and gas bubbles from liquids.

The degassers and the method of removing gases from liquids of this invention employ a means to contact a liquid containing dissolved gas or gas bubbles with a semipermeable membrane through which the gas is diffused, as do the degassers of the prior art. The advantages of this invention are obtained by using a membrane which is a fluorinated polymer having substituents of $-SO_3H$ or a salt thereof.

The fluorinated polymers useful in this invention have a backbone fluorocarbon chain with the $-SO_3H$ or salt thereof attached directly to a fluorinated carbon in the main fluorocarbon chain or to fluorocarbon side chains. Either the main chain or the side chains may contain oxygen atoms. The perfluoro polymers are preferred. More preferred is a copolymer of from 90 to 40% or, more preferably, 70 to 50% by weight tetrafluoroethylene and from 10 to 60% or, more preferably, 20 to 50% by weight, perfluoro (3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) in which the sulfonyl fluoride group is subsequently hydrolyzed to $-SO_3H$ or a salt thereof. The preferred polymers have an equivalent weight range of about 1100 to about 1400 with an equivalent weight of about 1100 being preferred.

The synthesis and processing of these polymers are known in the art as shown by U.S. 3,884,885 and are commercially available in the form of both flat films and tubes. Degassers can be made with either tubes or films, but tubes are preferred.

The best mode of using the invention is shown in cross section in Fig. 1. A chamber 1, adapted to be evacuated by connection of outlet 2 to a vacuum source, has coiled within it a tube 3 of semipermeable polymer. The tube is connected to inlet 4 and outlet 5 ports so that the liquid to be degassed can flow through the tubing. The tubing is loosely supported within the degasser by means of a cylindrical brush 6 which permits expansion and contraction of the tubing both in length and cross section due to pressure changes and the effect of liquids on the tubing. The degasser has a drain plug 7 to remove any liquid which passes through the tubing wall and is not evaporated.

It should be recognized that the surface area of membrane required for any particular application will be a function of rate at which a given volume of liquid moves past a unit area of the membrane, the pressure drop across the membrane, the temperature of the system and the amount of the particular gas to be removed from the liquid. The determination of the membrane area or residence time of the liquid within the degasser can be easily determined by those skilled in the art.

It should also be recognized that the membranes useful in this invention function as ion exchangers. Thus, any solvent system pumped through the degasser should be allowed to come to equilibrium with the membrane before any analytical work is begun.

Example

A gradient elution solvent system for a liquid chromatograph can be established in which a variable mixture of methanol and water is fed to a mixing chamber. Initially, the solvent is 100% methanol. The amount of water is increased continuously while the total flow rate is held constant so that after 10 minutes the solvent is 100% water. If both the water and the methanol are saturated with air, bubbles will be observed in the mixing chamber because the solubility of air in water-methanol mixtures is less than the solubility of air in methanol.

If this solvent system flows at the rate of 2.5 ml/min through a degasser of the type shown in Fig. 1 equipped with a membrane of the prior art, 1.5 meter of 0.1 cm i.d., 0.16 cm o.d. tubing of Teflon® FEP fluorocarbon resin and operated with a vacuum of 51 cm of mercury outside the tube wall, there is no noticeable decrease in bubble formation

in the mixing chamber.

If the solvent flows at the same rate through a similar degasser with the same vacuum but having a membrane of this invention, namely a Nafion ® perfluorosulfonic acid tubing type 815 with the same dimensions, no bubbles are generated in the mixer.

(Teflon ® and Nafion ® are registered trademarks of E.I. du Pont de Nemours and Company).

CLAIMS

1. An apparatus for removing gas from a liquid having means for contacting the liquid with a semi-permeable membrane through which the gas is removed, the said membrane comprising a fluorinated polymer having substituents of $-SO_3H$ or a salt thereof attached to fluorinated carbons.

2. The apparatus of Claim 1 wherein the membrane is a perfluoro polymer.

3. The apparatus of Claim 1 wherein the membrane is a copolymer of tetrafluoroethylene and perfluoro (3,6-dioxa-4-methyl-7-octenesylphonyl fluoride) in which the sulphonyl fluoride group is hydrolysed $-SO_3H$ or a salt thereof.

4. The apparatus of Claim 3 wherein the copolymer is made from 90 to 40% by weight tetrafluoroethylene and has an equivalent weight of about 1100 to about 1400.

5. The apparatus of Claim 4 wherein the copolymer is made from 70 to 50% by weight tetrafluoroethylene and has an equivalent weight of about 1100.

6. The apparatus of Claim 1 substantially as hereinbefore described with reference to the accompanying drawing.

7. A method for removing gas from a liquid which comprises contacting the liquid with a semi-permeable membrane through which the gas is removed, the said membrane being a fluorinated polymer having substituents of $-SO_3H$ or a salt thereof attached to fluorinated carbons.

8. The method of Claim 7 wherein the membrane is a perfluoro polymer.

9. The method of Claim 7 wherein the membrane is a copolymer of tetrafluoroethylene and perfluoro (3,6-dioxa-4-methyl-7-octenesulphonyl fluoride) in which the sulphonyl fluoride group is hydrolysed $-SO_3H$ or a salt thereof.

10. The method of Claim 9 wherein the copolymer is made from 90 to 40% by weight tetrafluoroethylene and has an equivalent weight of about 1100 to about 1400.

11. The method of Claim 10 wherein the copolymer is made from 70 to 50% by weight tetrafluoroethylene and has an equivalent weight of about 1100.

12. The method of Claim 7 substantially as hereinbefore described.

Printed for Her Majesty's Stationery Office by Croydon Printing Company Limited, Croydon Surrey, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.